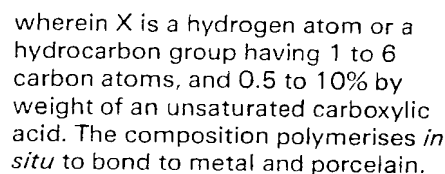


⁽¹²⁾ UK Patent Application ⁽¹⁹⁾ GB ⁽¹¹⁾ 2 086 914 A

- London, WC2A 1JQ

R' is selected from monovalent hydrocarbon groups

A is —



Certain of the chemical formulat(e) appearing in the printed specification were submitted in formal form after the date of filing. This print embodies corrections made under Section 117(1) of the Patents Act 1977.

SPECIFICATION

Denture-base Resin Composition and Method for Using the Same

The present invention is concerned with a denture-base resin composition.

As is well-known, artificial teeth having a metal base is more tough, yet less breakable as compared with those composed exclusively of methyl methacrylate resin. The denture-base can then be made so thin that the resulting denture produces a more natural "feel" to the patient, and in service, is free from any water absorption properties, and has high dimensional stability. In addition, the dentures of the above-mentioned type has numerous advantages, its base has no or little irritating effect; it is impermeable to saliva and mouth tissues to the extent that it will not become unsanitary, it has good thermal conductivity without sacrificing a kind of sensitivity to temperature or taste, and it has sufficient strength to resist all normal masticating stresses.

At the present time, metal materials that are enjoying any degree of success for denture-base materials include gold-alloys, gold/silver/palladium alloys, platinum alloys, cobalt/chromium alloys, nickel/chromium alloys, 18-8 stainless-steel wrought alloys etc. Among these alloys, the cobalt/chromium or nickel/chromium alloys are becoming widespread since they are light in weight, say, about one half of the density of the gold alloys, and are very strong, say, about twice the Young's modulus of elasticity. In addition, they are inexpensive and excel in the resistance to discolouration. Artificial teeth used with these metal bases include porcelainous and resinous teeth; however, preference is generally given to the porcelainous teeth in view of hardness, wear resistance, harmlessness etc.

In some cases, the metal base may be formed as an integral piece from a metal. In most of the dentures having a metal base that are now available, an alveolous portion for fixing artificial teeth in place and a portion exposed to the inside of the cheek within the oral cavity are composed of a resin while a portion on the palate side is formed of a metal. Thus, advantage is taken of both metal and resin.

A methyl methacrylate resin is now widely used as a denture-base resin material. However, this methyl methacrylate resin has no chemical adhesion to dental metals or porcelainous teeth at all. Although various proposals have been made to establish a mechanical connection between the resin and the metal or porcelainous teeth, there is still left much to be desired. Typically, when the denture receives external forces such as masticating stresses in the oral cavity during use, the junction between the metal and the resin cracks to cause separation of one from the other, thus resulting in discolouration and contamination of the resin, with emission of an offensive odour.

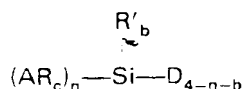
The problem of the mechanical connection inevitably renders the denture design and the casting work complicated and difficult. In some cases, polishing of the artificial teeth may cause breakage of a thin portion of the junction between it and the metal. Use of a retention bead in the junction imposes a certain limitation upon the colour tone of the denture. As there is no choice but to cover the mucous surface of the denture base with a metal, it is impossible to effect lining of resin, often referred to as the so-called relining, even when engagement of the base with the metal becomes deteriorated.

When dentures are fabricated from porcelainous teeth and conventional denture-base resin, reliance is put upon either retainer means comprising gold pins set in the surface of the denture base or mechanical retainer means using holes, since the porcelainous teeth do not show any chemical adhesion to the base resin at all. This often causes breakage of the porcelainous teeth due to the concentration of stresses to part thereof held by said retainer means, this resulting in disengagement of the dentures from a given place in the oral cavity during use, as reported in literature.

In addition, accumulation of the mouth fluids and occurrence of bacteria take place in the crevices in the interface of the resin base and the porcelainous teeth during use, leading to tarnishing of the artificial teeth and emission of an offensive odour. With a view to eliminating the above-mentioned defects, it has attempted to make a chemical bond between the porcelainous teeth or metal and the base resin material. It has been proposed, for example, the surface of a metal is etched with an inorganic acid, coated with adhesives and laminated with a methacryl resin. An alternative process using 4-methacryloxyethyl trimellitate has also been reported. However, these processes often offer several problems; they result in a considerable drop in efficiency and marked variations in the adhesion to the cobalt/chromium alloys and the nickel/chromium alloys. In these processes, any adhesion to the porcelainous teeth is not obtained at all.

In order to bond the base resin to the porcelainous teeth, it has been proposed to incorporate a silane compound into the methyl methacrylate. With this process, it is possible to bond the base to the porcelainous teeth, but it is difficult to bond the base to the metal. There are also considerable variations in the adhesive force.

According to the present invention, there is provided a denture-base resin composition comprising a methyl methacrylate monomer containing 0.5 to 20% by weight of a silane compound having the general formula:



in which

D: a hydrolyzable group

n: an integer of 1, 2 or 3

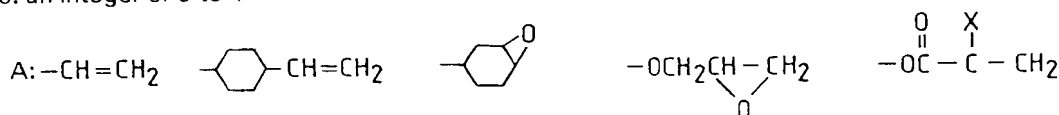
b: an integer of 0, 1 or 2

5 n+b: an integer of 1, 2 or 3

R' is selected from monovalent hydrocarbon groups

R: an alkylene group having 1 to 4 carbon atoms

c: an integer of 0 to 1



10 wherein

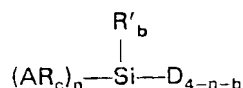
X: a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, and mixed with 0.5 to 10% by weight of an unsaturated carboxylic acid.

Thus the present invention provides a novel denture-base resin composition having chemical adhesion with respect to porcelainous teeth and dental cobalt or nickel/chromium alloys without having an adverse influence on the excellent working and physical properties of a denture-base methyl methacrylate material that is widely available in dentistry. The novel composition of the present invention can be put to use without recourse to any mechanical retainer means that are used in the prior art for the purpose of holding the porcelainous teeth and the metal in place.

According to the present invention, the physical and chemical properties, such as resistances to folding and flexion, impact and solvents of the denture-base methacryl material that is widely available in dentistry can substantially be improved without sacrificing the numerous advantages thereof, such as good appearance, working properties and adhesion to resin teeth. In accordance with one embodiment of the present invention, a composition containing 50 ppm of hydroquinone, can be stored for two or more years without curing.

More specifically, the denture-base composition of the present invention contains a liquid component obtained by incorporation of 0.5 to 20% by weight of a particular silane compound (to be defined later) and 0.5 to 10% by weight of an unsaturated carboxylic acid into a methyl methacrylate monomer. This liquid component is mixed with a methyl methacrylate polymer in a weight ratio of 1:3 to 3:1 and the resultant mixture is shaped into a denture form in a conventional manner known in dentistry. Fabrication of the denture comprising a metal plate and porcelainous teeth with such a composition will now be explained. When the resin dough is placed under pressure and preheated, the unsaturated carboxylic acid first produces an effective action, say, cleaning or etching effect, on the resin-bonded surface of the metal or porcelainous teeth to activate the bonded surface. Subsequent polymerisation of the methyl methacrylate monomer causes the remaining components to be simultaneously polymerised, thereby making a firm bondage. The actions of these components are very effective since they are exerted without causing the bonded surface to be exposed to atmosphere.

The particular silane compound referred to herein is expressed by the general formula:



wherein

D: a hydrolyzable group

n: an integer of 1, 2 or 3

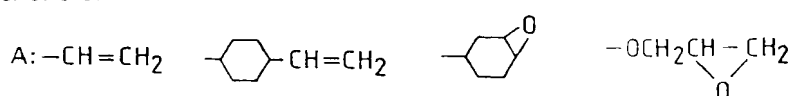
b: an integer of 0, 1 or 2

n+b: an integer of 1, 2 or 3

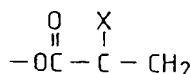
R': a group selected from the group consisting of monovalent hydrocarbon groups

R: an alkylene group having 1 to 4 carbon atoms

c: an integer of 0 or 1



or



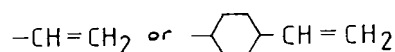
50 wherein

X: a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms.

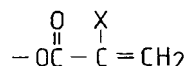
In the above-mentioned general formula, D may be any hydrolyzable group. The number of the group D in the silane compound may be 1, 2 or 3, but preference is given to 3. The group D may be, for instance, methoxy, ethoxy, propoxy, isopropoxy or the like group. The group R' may be any monovalent hydrocarbon groups, including methyl, ethyl, propyl, butyl and the like group. The methyl group is

recommendable. The latter b may be 1, 2 or 0. The number of the group ARc may be 1, 2 or 3. In other words, n may be 1, 2 or 3 but should preferably be 1. The group represented by R is a divalent C_{1-4} alkylene group bonded to a silicon atom, such as methylene, ethylene, trimethylene, propylene and the like group. c may be 1 or 0 that means the absence of the group R . A is bonded to the group R except the case where it is directly bonded to a

silicon atom, say, $c=0$. When $c=0$, A stands for



The letter X in the group



may be a C_{1-8} hydrocarbon group. In this case, an ester group is present in the compound. For instance, X includes methyl, ethyl, isopropyl, butyl and the like group.

Some of the compounds falling under the foregoing definition are commercially available, including γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, vinyltriethoxysilane, β -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane, vinyl-tris(β -methoxyethoxy)-silane. Among these compounds, use is most preferably made of γ -methacryloxypropyltrimethoxysilane.

The unsaturated carboxylic acids used in the present invention may be both an unsaturated monocarboxylic acid and an unsaturated polycarboxylic acid. For instance, use is made of acrylic, methacrylic, crotonic, linolic, undecenoic, β -2-furilacrylic, cinnamic, sorbic, fumaric, maleic and citraconic acids.

Following is a description by way of example only of methods of carrying the invention into effect.

The following examples were conducted under the common conditions set forth below. For comparison, these examples are summed up in terms of adhesion and folding and endurance to flexing in the following Table.

As a powdery component, use was made of a PMMA polymer (polymethyl methacrylate; particle size: 120—200 Tyler meshes) containing 0.1% B.P.O. (benzoyl peroxide). The PMMA powdery component was mixed with the liquid component specified in the Examples by a mixing ratio (by weight) of 1:2 to form a dough. The dough was prepolymerised at 70°C for 30 minutes in the conventional manner, and was polymerized and heated at 100°C for 30 minutes. As mentioned above, these results are set forth in the Table. From these results, it has been found that the products according to the present invention are superior in the adhesion and physical properties to samples obtained from a commercially available monomer.

In examination of the adhesion of the product with respect to a metal, a 5×5×5 mm mound of wax was formed on the centre of a 10×10×2 mm metal test piece that was polished with a chromium oxide abrasive, and was charged in a plaster mold in the conventional manner. After setting of the plaster, the wax was flushed out. The thus formed negative model was washed and filled with a resin sample for polymerization.

In order to measure the adhesion of the product with respect to porcelainous teeth, a test in accordance with JIS T 6511 Test Standard was used. When the concentration of the silane compound is less than 0.5% by weight, the adhesion power with respect to the porcelainous teeth is less than 5 kg, which means that there is a fear that disengagement of the porcelainous teeth takes place in use. At a concentration of the silane compound exceeding 20% by weight, the product has a flexion of more than 6 mm under 5 kg load in the folding and flexion endurance test, and does not meet JIS T 6501 Standard so that it is no longer used for the practical purpose. When the concentration of the unsaturated carboxylic acid is less than 0.5% by weight, the adhesion power of the product with respect to the cobalt/chromium alloy is less than 40 Kg/cm². In this case, the unsaturated carboxylic acid produces no effect. At a concentration of more than 10% by weight, the product has a flexion endurance of less than 5 Kg, and is not used for the practical purpose. Thus, best results are obtained when the upper and lower limits of the silane compound and the unsaturated carboxylic acid are 0.5—20% by weight and 0.5—10% by weight, respectively.

The specific examples of the present invention are given below. The adhesion power and endurance to flexing measured in each example are summed up in the Table. However, it will be understood that the present invention is not limited to the figures given in the examples.

Example 1

Use was made of a liquid composition prepared by adding 50 ppm of hydroquinone to a mixture of:

5	Methyl methacrylate monomer	90 parts	5
	<i>p</i> -methacryloxypropyltrimethoxysilane	6 parts	
	Undecenoic acid	4 parts	

Example 2

In place of undecenoic acid in Example 1, methacrylic acid was employed.

Example 3

10 Use was made of a liquid composition prepared by adding 100 ppm of butylated hydroxyparatoluene to a mixture of: 10

Methyl methacrylate monomer	96 parts
<i>p</i> -methacryloxypropyltrimethoxysilane	3 parts
Acrylic acid	1 part

Example 4

15 Use was made of a liquid composition prepared by adding 50 ppm of hydroquinone to a mixture of:

20	Methyl methacrylate monomer	90 parts	20
	Ethylene glycol dimethacrylate	1 part	
	<i>p</i> -methacryloxypropyltrimethoxysilane	6 parts	
	Citraconic acid	3 parts	

Example 5

Use was made of a liquid composition prepared by adding 50 ppm of hydroquinone to a mixture:

25	Methyl methacrylate	91 parts	25
	<i>p</i> -methacryloxypropyltrimethoxysilane	5 parts	
	4-methacryloxyethylenetrimellitate	3 parts	

Example 6

In Example 3, *p*-glycidoxypropyltrimethoxysilane was used as the silane compound.

Example 7

30 In Example 3, vinyltriethoxysilane was used as the silane compound. 30

Example 8

In Example 3, β -phenylethyltrimethoxysilane was used as the silane compound.

Example 9

35 In Example 3, 2% by weight of dimethylparatoluidine were added to the methyl methacrylate monomer. The resultant liquid composition was allowed to stand at room temperature without heating. 35

Example 10

In Example 3, the acrylic acid was not used.

Example 11

In Example 3, the silane compound—*p*-methacryloxypropyltrimethoxysilane—was not used.

Example 12

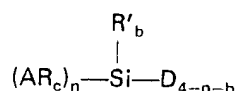
40 Use was made of a commercially available denture-base material. 40

Table

Examples	Adhesion			
	Ni/Cr Alloys (Kg/cm ²)	Co/Cr Alloys (Kg/cm ²)	Porcelaneous Teeth (without any retainer) JIS T6511 (Kg)	Folding and Flexion Endurance Strength JIS T6501 (Kg)
(1)	180	167	35	8.0
(2)	210	220	38	9.0
(3)	213	210	35	8.5
(4)	190	187	37	8.0
(5)	210	214	35	8.5
(6)	185	174	35	7.5
(7)	158	135	33	8.0
(8)	165	121	35	8.0
(9)	130	105	28	8.0
(10)	35	40	32	8.0
(11)	20	15	0	5.5
(12)	0	0	0	5.5

Claims

1. A denture-base resin composition comprising a methyl methacrylate monomer containing 0.5 to 20% by weight of a silane compound having the general formula:



in which

D: a hydrolyzable group

n: an integer of 1, 2 or 3

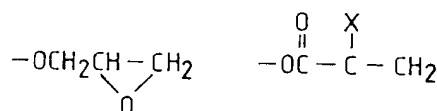
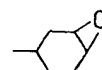
b: an integer of 0, 1 or 2

n+b: an integer of 1, 2 or 3

R': is selected from monovalent hydrocarbon groups

R: an alkylene group having 1 to 4 carbon atoms

c: an integer of 0 to 1



wherein

X: a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms, and mixed with 0.5 to 10% by weight of an unsaturated carboxylic acid.

2. A composition as claimed in claim 1 in which the unsaturated carboxylic acid used is an unsaturated monocarboxylic acid.

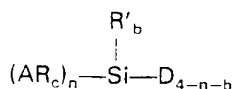
3. A composition as claimed in claim 2, in which the unsaturated carboxylic acid is an unsaturated polycarboxylic acid.

4. A composition as claimed in any one of claims 1 to 3, in which the methyl methacrylate monomer contains 0.1 to 5% by weight of a cross-linking agent.

5. A composition as claimed in any one of claims 1 to 4, in which the methyl methacrylate monomer contains 0.1 to 2.0% by weight of amines set at normal temperatures.

6. A composition as claimed in claim 1 and substantially as described in any one of the specific examples hereinbefore set forth.

7. A method of using the composition claimed in claim 1 which method comprises mixing a liquid denture-base resin composition comprising a methyl methacrylate monomer containing 0.5 to 20% by weight of a silane compound having the general formula:



wherein

D: a hydrolyzable group

n: an integer of 1, 2 or 3

b: an integer of 0, 1 or 2

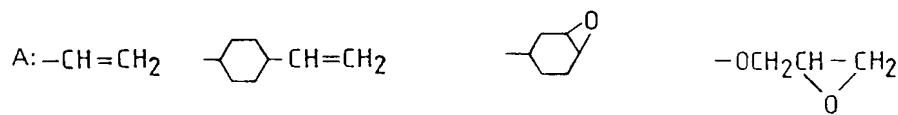
5 n+b: an integer of 1, 2 or 3

R': is selected from monovalent hydrocarbon groups

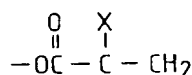
R: an alkylene group having 1 to 4 carbon atoms

c: an integer of 0 or 1

5



10



wherein

5 X: a hydrogen atom or a hydrocarbon group having 1 to 6 carbon atoms and mixed with 0.5 to 10% by weight of an unsaturated carboxylic acid, with a powdery methyl methacrylate polymer in a mixing ratio of 1:3 to 3:1.

15

